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# ANIONIC ADSORPTION ON THREE SULPHIDE MINERALS

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ANIONIC ADSORPTION ON THREE SULPHIDE MINERALS

by

Hugh P. Dibbs\*

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SYNOPSIS

A study has been made of anionic adsorption on pyrite, sphalerite and galena from solutions of sodium sulphide, labelled with sulphur-35, and phosphoric acid, labelled with phosphorus-32. It was found that the three minerals exhibited similar behaviour in each solution. The dependence of this behaviour on pH and on the concentration of the test solution has been examined.

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Direction des mines

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ADSORPTION ANIONIQUE PAR TROIS MINÉRAUX SULFURÉS

par

Hugh P. Dibbs\*

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RÉSUMÉ

L'auteur a étudié l'adsorption anionique sur la pyrite, la sphalérite et la galène à partir de solutions de sulfure de sodium, marqué au soufre 35, et d'acide phosphorique, marqué au phosphore 32. Il a constaté que les trois minéraux en question se comportaient de la même façon dans chaque solution. L'auteur a examiné de quelle façon ce comportement pouvait dépendre du pH et de la concentration de la solution analysée.

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## INTRODUCTION

Radioactive tracers have been used widely as an aid in studying adsorption on minerals in laboratory-scale investigations (1, 2) and also as a means of labelling particular minerals in flotation and milling circuits (3). Most of these adsorption studies, however, have been concerned with inorganic cations and less attention has been devoted to anionic adsorption. In order to investigate further this latter aspect of mineral adsorption, the present study was made of anionic adsorption from solutions of sodium sulphide, labelled with sulphur-35, and from solutions of phosphoric acid, labelled with phosphorus-32, on three sulphide minerals: pyrite, sphalerite, and galena.

## EXPERIMENTAL METHOD

Sodium sulphide labelled with sulphur-35 was obtained from the Radiochemical Centre, Amersham, England. It was dissolved in an appropriate volume of distilled water to make an approximately  $10^{-3}$  M  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  stock solution with a specific activity of about 2.5  $\mu\text{c}/\text{ml}$ . Because of the instability of aqueous solutions of sodium sulphide in the presence of air, this stock solution was stored under argon in an all-glass apparatus. Aliquots of the solution, for test purposes, were transferred from the stock

solution by means of argon pressure. Preliminary work had indicated that sodium sulphide solutions could be kept in this manner for at least a week with little decomposition. For adsorption measurements, 8 ml of the active solution, after suitable pH adjustment with 0.01 N  $\text{H}_2\text{SO}_4$  or 0.01 N NaOH, were contacted with 0.5 g of the sulphide mineral in a glass-stoppered tube and agitated in a rotary shaker for a predetermined time. When the shaking was completed, the mineral was filtered on a ground-glass frit, using a water pump, and washed a number of times with distilled water. The powder was then dried with acetone, placed in a small planchette, and counted in a position of fixed geometry with respect to a thin ( $1.8 \text{ mg/cm}^2$ ) end-window Geiger counter. Since sulphur-35 has a half-life of 87.1 days, no correction for radioactive decay was necessary, as each solution was used for not longer than a week.

A similar technique was employed in the study of adsorption from phosphoric acid solutions (specific activity about  $2\mu\text{c/ml}$ ), except that it was not necessary to guard against any decomposition of the solution. As the half-life of phosphorus-32 is only 14.3 days, corrections for decay were made when necessary. The high-specific-activity phosphoric acid stock solution was obtained from Atomic Energy of Canada Limited, Ottawa.

The sulphide minerals used in this work were selected from naturally occurring crystals obtained from the Geological Survey of Canada. They were ground and sized, the mesh fractions employed being: pyrite, -48+65 mesh; galena, -35+65 mesh; and sphalerite, -35+65 mesh. The results of a chemical analysis of the samples are given in Table 1.

TABLE 1  
Chemical Analysis of Pyrite, Sphalerite and Galena

%	Pyrite	Sphalerite	Galena
Fe	45.9	9.4	
S	53.02	34.9	15.32
Zn		52.2	1.76
Pb			76.3
SiO <sub>2</sub>	0.44	0.24	1.97
Insol.	0.12	0.44	3.75

All the experimental results were obtained at room temperature.

## DETAILS OF TESTS

### Experiments with Sodium Sulphide Solution

#### (a) Labelled Sodium Sulphide

The first variable investigated was the influence of contact time on the amount of sulphur-35 adsorbed by the minerals. For pyrite it was found, at all the pH values and concentrations examined (pH, 6.6 to 10.9; concentration,  $2.5 \times 10^{-3}$  M to  $5 \times 10^{-5}$  M), that equilibrium was attained very rapidly and that increasing the contact time beyond about two minutes led to no further increase in sulphur-35 adsorption. This is shown for pyrite in Fig. 1 at pH 10.9 and pH 8.1. For the other two minerals shown in the same figure, no sign of saturation is apparent at pH 10.9, but for sphalerite, at pH 7.5, a behaviour comparable to that of pyrite is evident.

The effect of pH on the amount of sulphur-35 adsorbed for each of the three minerals, at a given sodium sulphide concentration, is shown in Fig. 2 for concentrations of  $0.33 \times 10^{-3}$  M and  $1 \times 10^{-3}$  M. This effect follows a regular pattern in that the amount of sulphur-35 adsorbed increases with decreasing pH. For pyrite, the effect of sodium sulphide concentration was examined over a wider range of concentrations at four different pH values. This is illustrated in Fig. 3, where it will be seen that an increase of concentration above about  $10^{-3}$  M did not further increase the amount of sulphur-35 adsorbed.



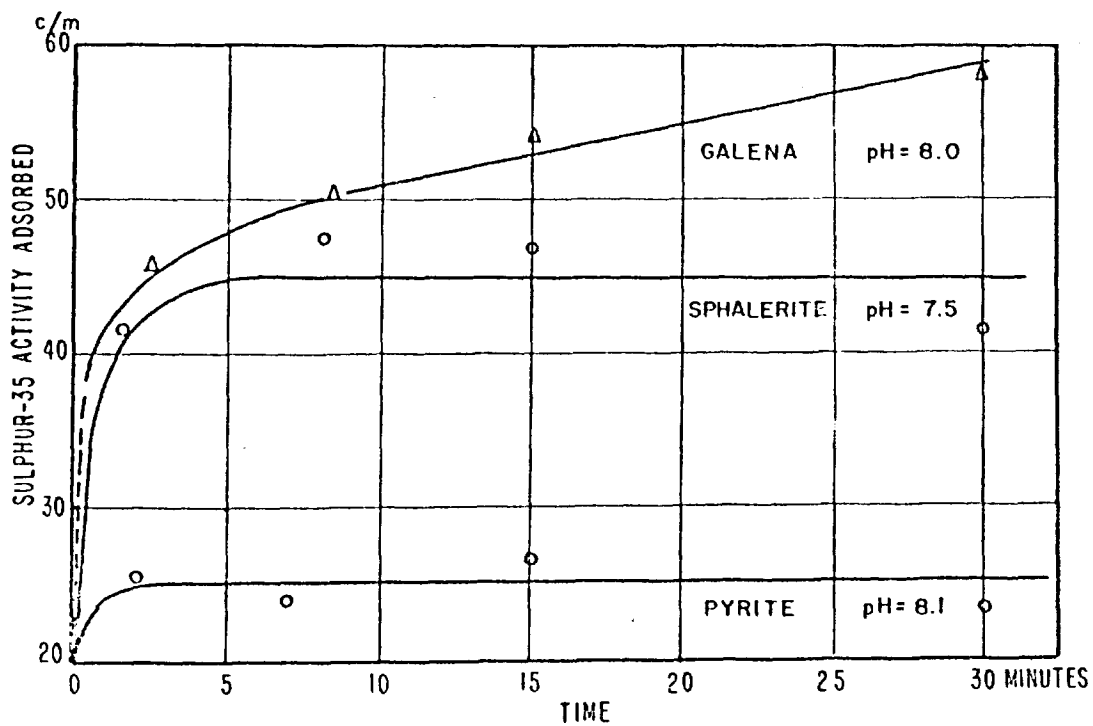
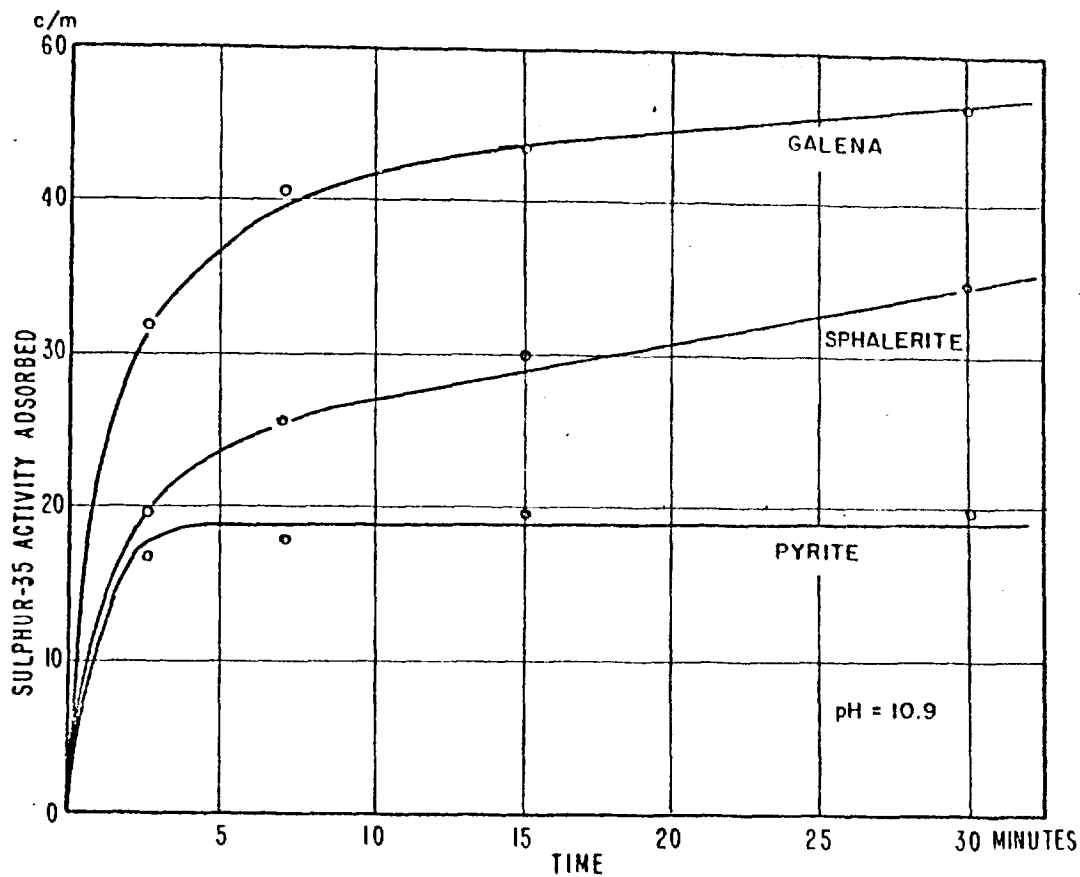


FIGURE 1 - TIME-DEPENDENCE FOR SULPHUR-35 ADSORPTION FROM  $1 \times 10^{-3} \text{ M Na}_2\text{S} \cdot 9 \text{ H}_2\text{O}$  SOLUTION.

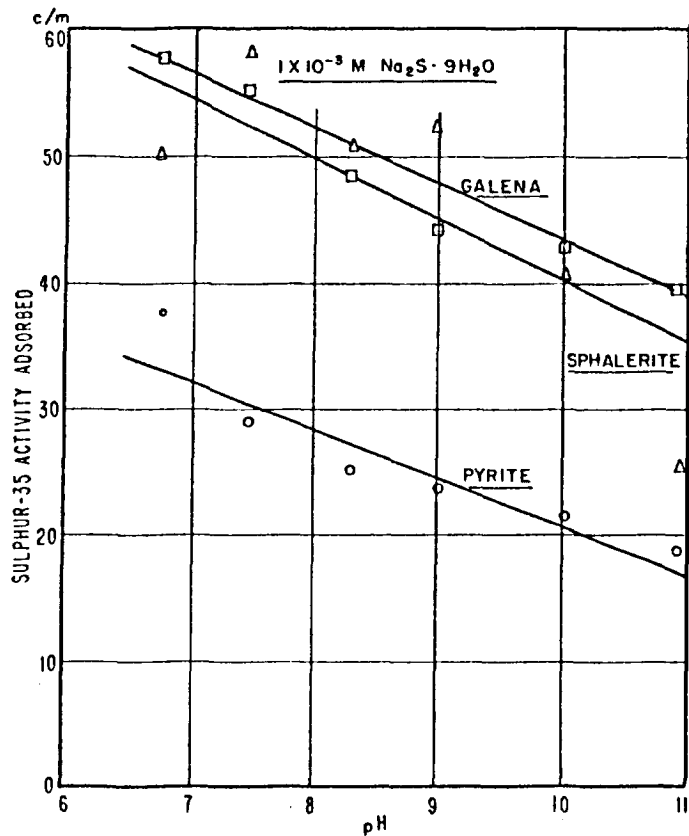
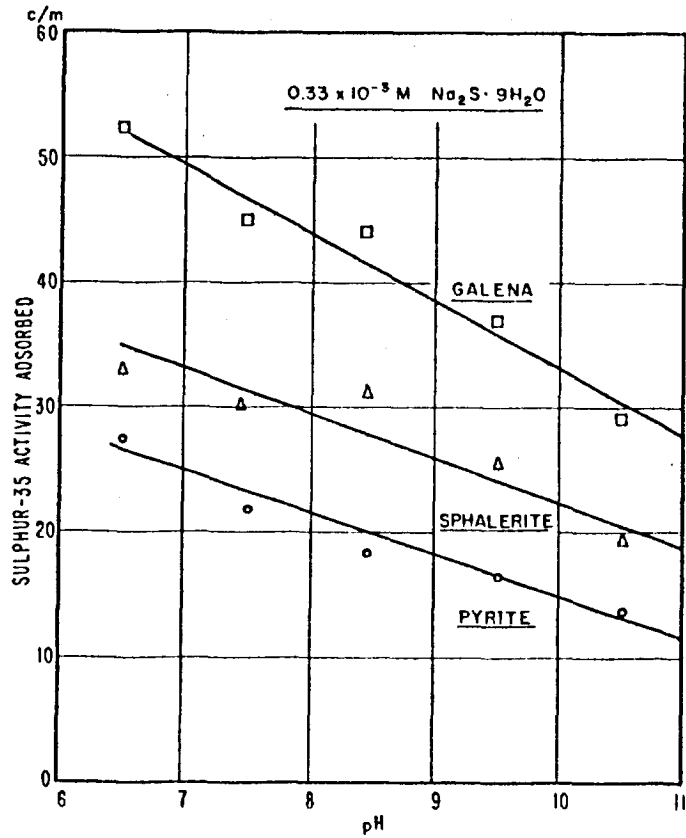


FIGURE 2 - ADSORPTION OF SULPHUR-35 ON GALENA, SPHALERITE & PYRITE AS A FUNCTION OF pH (5-MINUTE CONTACT).

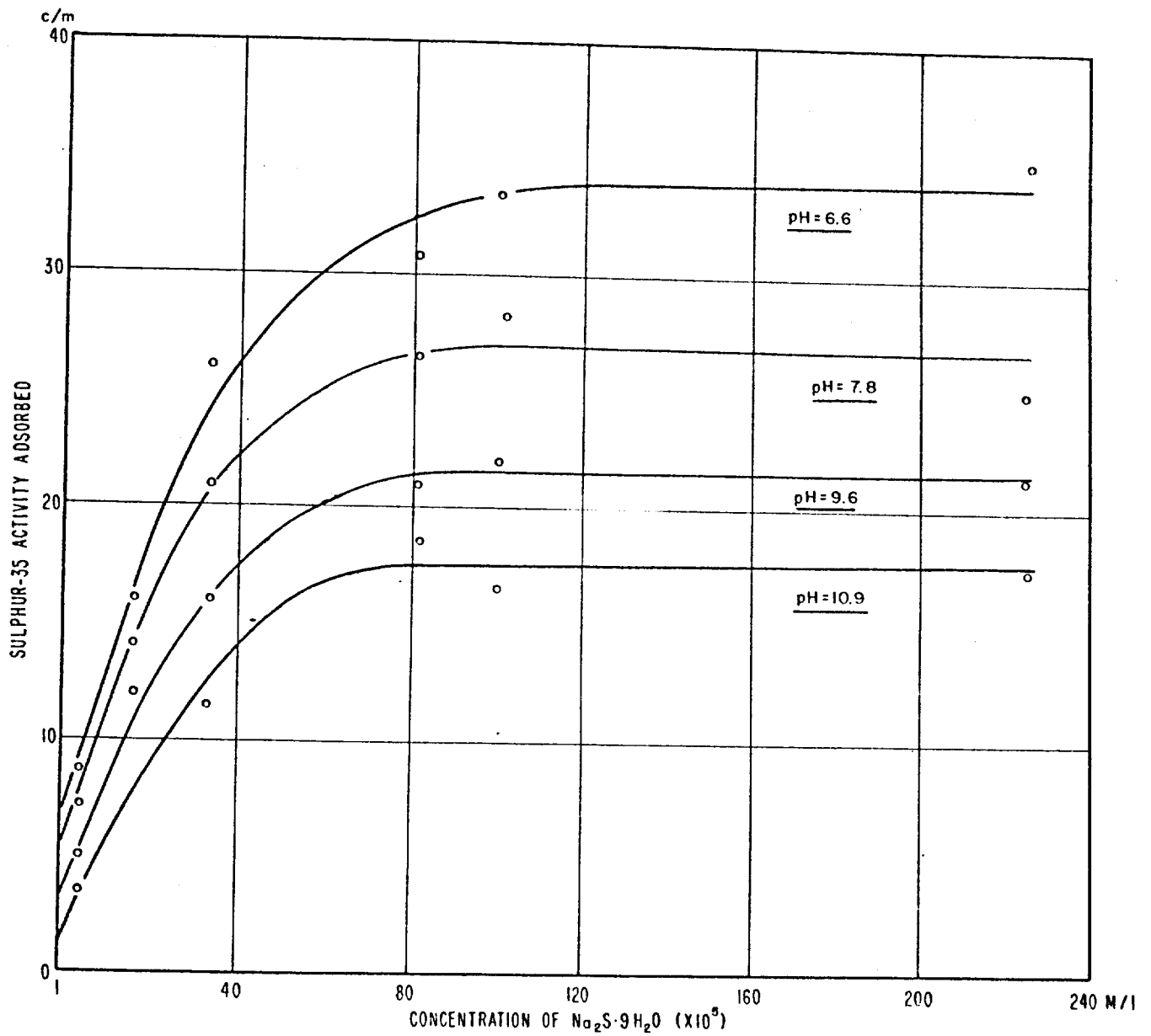


FIGURE 3 - DEPENDENCE OF SULPHUR-35 ADSORPTION ON PYRITE UPON  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  CONCENTRATION.

A rough estimate of the amount of sulphur-35 adsorbed was made by adding an aliquot of the active solution of known specific activity to 0.5 g of the mineral, allowing it to dry, and counting. It was found that one count per minute (c/m) corresponded approximately to the adsorption of 0.25  $\mu\text{g}$  of sulphur in the cases of pyrite and sphalerite and of 0.16  $\mu\text{g}$  of sulphur in the case of galena.

(b) Activated Pyrite and Inactive Sodium Sulphide

The adsorption results described, which were obtained using active sulphide in solution, could arise from sulphide ion exchange between the mineral and the solution and/or adsorption. In order to check this question for pyrite, 5 g of the mineral were irradiated with thermal neutrons to produce  $\text{Fe}^{59}\text{S}_2^{35}$ . The reverse process could then be examined using an inactive  $1 \times 10^{-3}$  M sodium sulphide solution. It was intended to perform this experiment at approximately pH 7 where the greatest exchange should occur (see Fig. 2). However, it was found that a blank determination using water of this pH resulted in some activity passing into solution. This activity probably arose from the presence of oxidized patches on the pyrite surface, or from traces of very finely divided pyrite going into solution. A number of washings were necessary to reduce the activity formed in this manner to a value comparable to background. When this was achieved, 0.5 g of the active pyrite was agitated with 8 ml of an inactive,  $1 \times 10^{-3}$  M  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  solution at pH 7.5. After

5 min of agitation a 6-ml sample of the solution was oxidized to sulphate by the method of Bethge (4), then evaporated to dryness on a planchette, and counted with the end-window Geiger counter. The same sample was then examined on a 100-channel gamma-ray spectrometer for iron-59 activity. For a number of samples it was found that the iron-59 peak height from the spectrometer measurement and the beta count obtained using the Geiger counter bore the same ratio to each other, which was also the same as the ratio found from the pyrite samples washed with water and oxidized in the same way. This similarity of ratio indicates that agitation of the active pyrite with inactive sodium sulphide resulted in little or no sulphide ion exchange.

#### Experiments with Labelled Phosphoric Acid

The time-dependence for adsorption on the three minerals from a  $0.85 \times 10^{-3}$  M phosphoric acid solution is shown in Fig. 4 at pH 4.1 and pH 8.2. These curves indicate that the rate of attainment of equilibrium is much slower than for a sodium sulphide solution of similar concentration, with only a gradual approach to equilibrium, even at the higher pH levels.

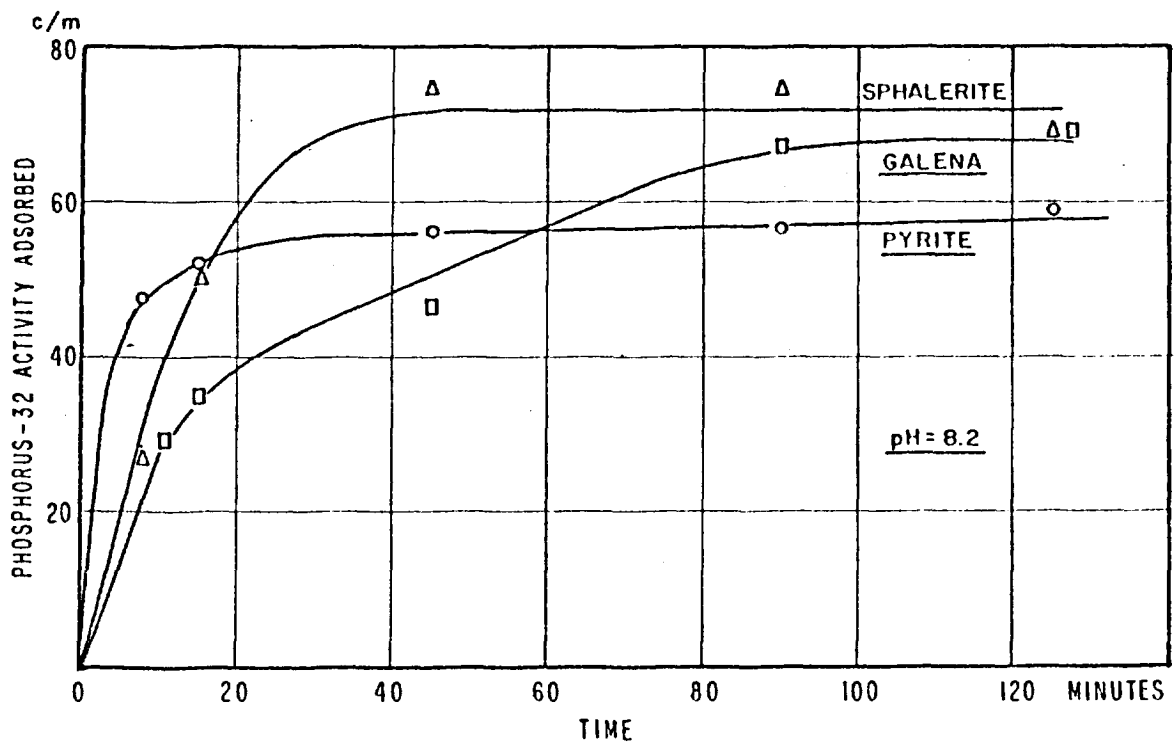
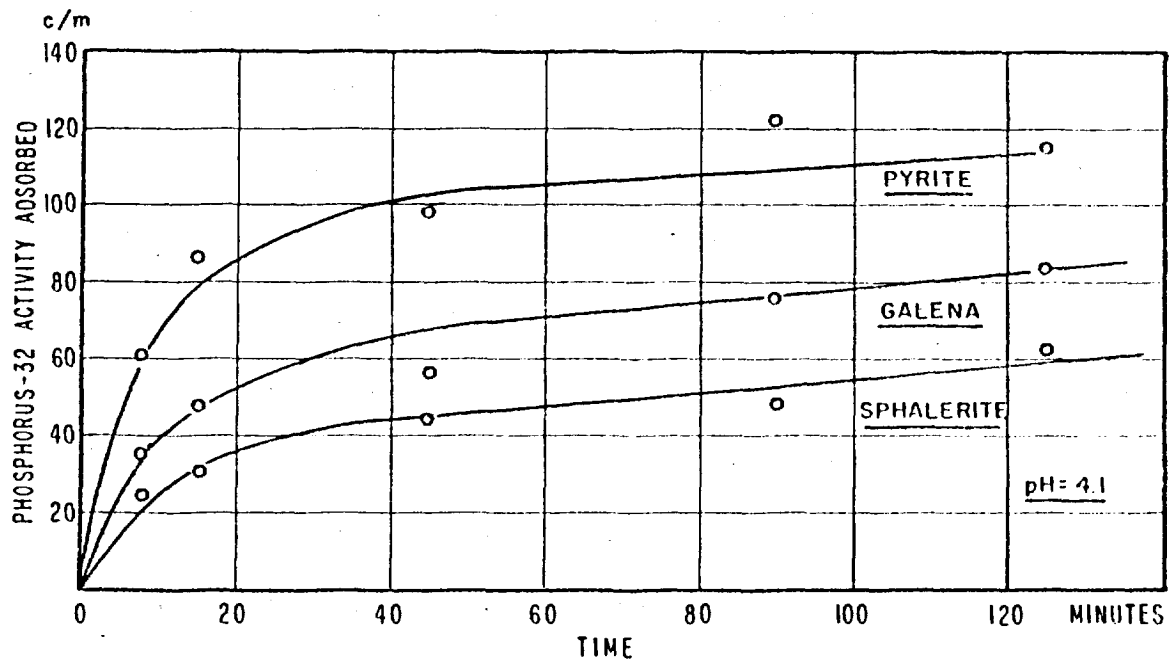


FIGURE 4 - TIME-DEPENDENCE FOR PHOSPHORUS-32 ADSORPTION FROM  $0.85 \times 10^{-3} \text{ M H}_3\text{PO}_4$  SOLUTION ON SPHALERITE, PYRITE & GALENA.

The effect of pH on the amount of phosphorus-32 adsorbed, at a fixed phosphoric acid concentration, was very similar for all three minerals, giving rise to a characteristic hump-shaped curve. This is shown at a phosphoric acid concentration of  $0.28 \times 10^{-3}$  M for galena and sphalerite in Fig. 5 and for pyrite in Fig. 6. Very similar curves to those in Figs. 5 and 6 were found for a  $0.85 \times 10^{-3}$  M phosphoric acid solution, with almost the same amount of phosphorus-32 activity adsorbed.

The adsorption of phosphorus-32 from a solution containing both inactive sodium sulphide ( $0.33 \times 10^{-3}$  M) and active phosphoric acid ( $0.25 \times 10^{-3}$  M) is shown by a dashed line in Figs. 5 and 6. It will be seen that there is a marked reduction in the amount of phosphorus-32 adsorbed by the three minerals. This effect is undoubtedly related to the much more rapid rate of adsorption from sulphide solutions, as compared to phosphoric acid solutions, which limits the sites available for phosphorus-32 adsorption.

Using the same technique as with the sodium sulphide solution, it was found that one count per minute corresponded approximately to the adsorption of  $0.28 \mu\text{g}$  of phosphoric acid on the minerals.

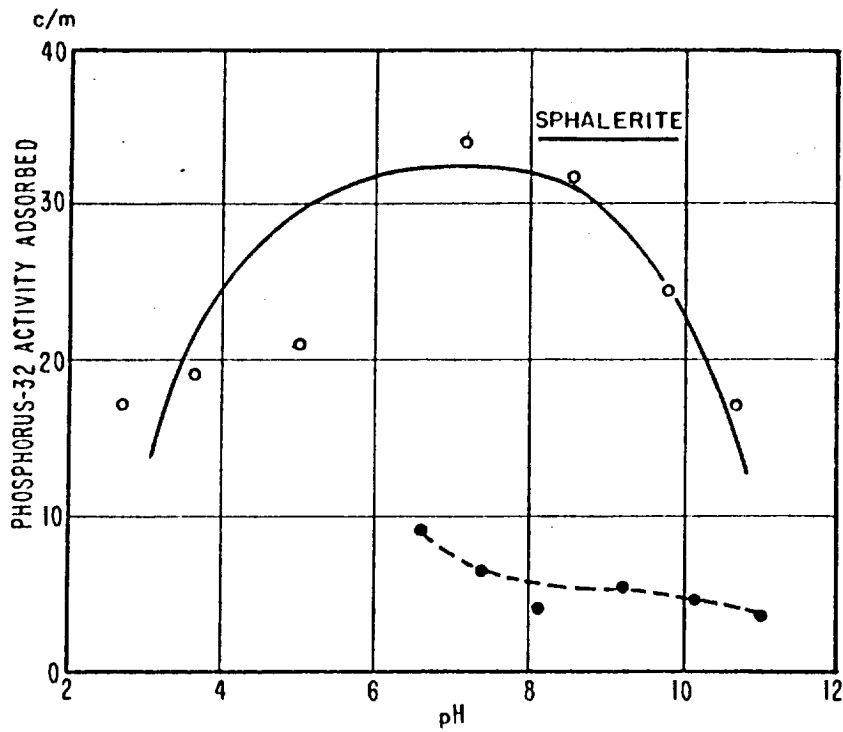
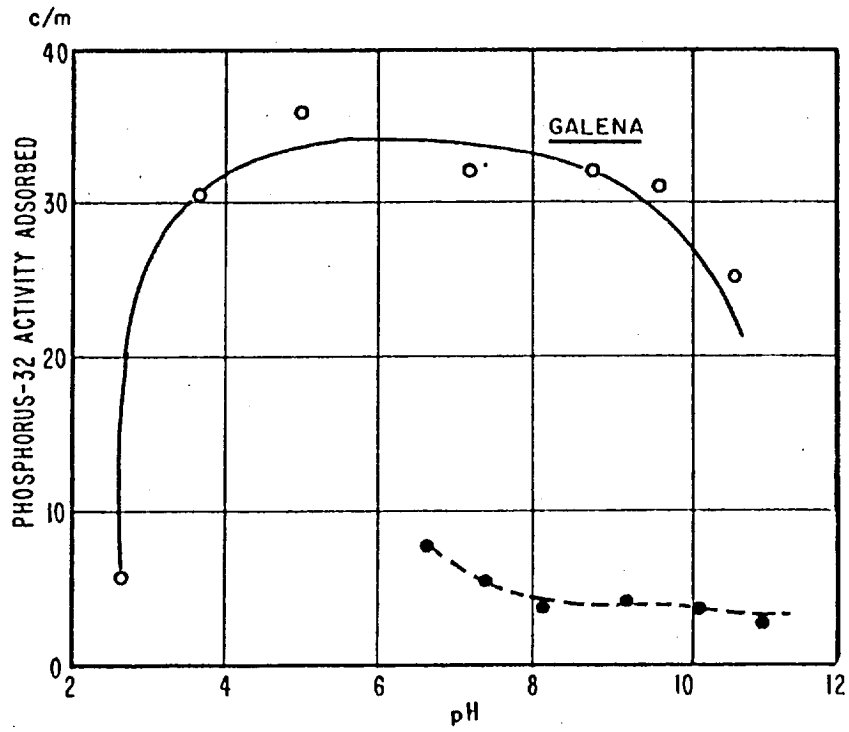


FIGURE 5-ADSORPTION OF PHOSPHORUS-32 ON GALENA & SPHALERITE AS A FUNCTION OF pH.

—○—  $0.28 \times 10^{-3} M H_3PO_4$ ; ---●---  $0.25 \times 10^{-3} M H_3PO_4 + 0.33 \times 10^{-3} M Na_2S \cdot 9H_2O$



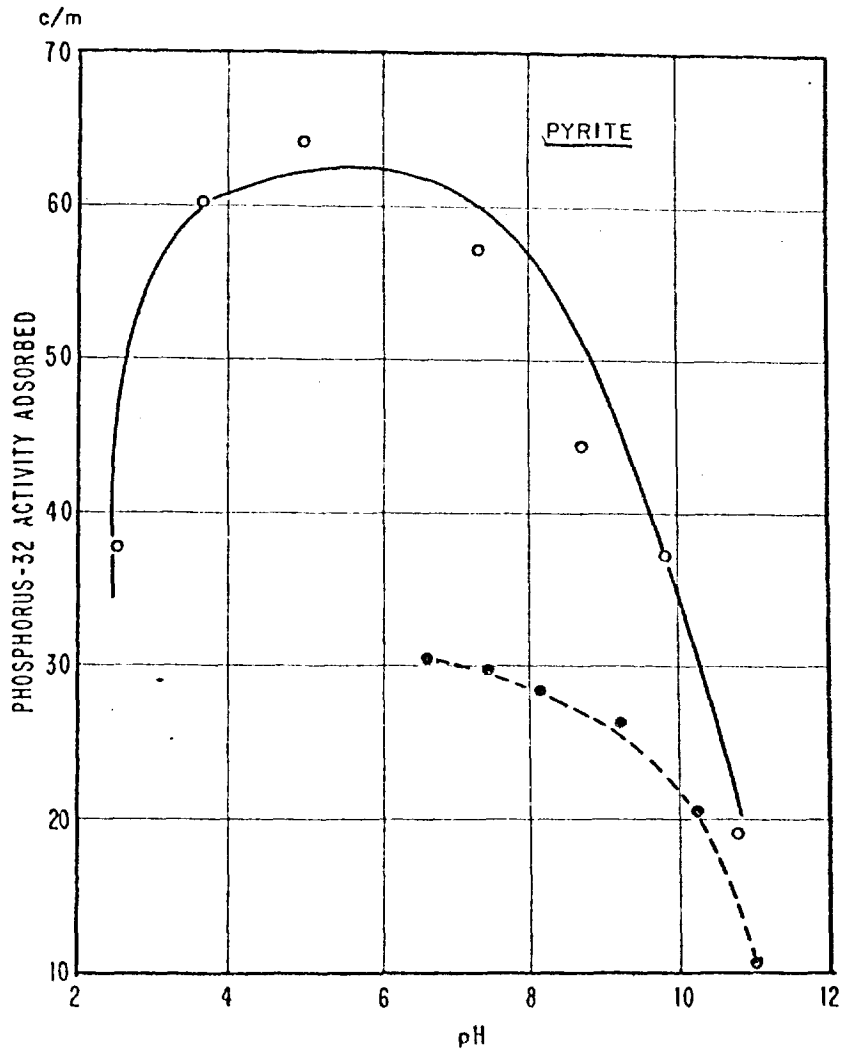


FIGURE 6- ADSORPTION OF PHOSPHORUS-32 ON PYRITE AS A FUNCTION OF pH.

---●--- 0.25 X 10<sup>-3</sup> M H<sub>3</sub>PO<sub>4</sub> + 0.33 X 10<sup>-3</sup> M Na<sub>2</sub>S · 9 H<sub>2</sub>O

—○— 0.28 X 10<sup>-3</sup> M H<sub>3</sub>PO<sub>4</sub>

DISCUSSION

In an aqueous solution of sodium sulphide, equilibrium is established between the sodium sulphide and dissolved sulphur in the form of  $S^{--}$ ,  $HS^-$  and  $H_2S$ . This equilibrium is controlled by the two dissociation constants of  $H_2S$ , namely:  $K_1 = 10^{-7}$ , and  $K_2 = 2 \times 10^{-15}$  (5). From these dissociation constants and the concentration of sodium sulphide, it is possible to calculate the concentration of  $S^{--}$ ,  $HS^-$  and  $H_2S$  present at any given pH. This is shown in Table 2 for a  $1 \times 10^{-3}$  M  $Na_2S \cdot 9H_2O$  solution.

TABLE 2

Dependence on pH of the Concentration of  $S^{--}$ ,  $HS^-$  and  $H_2S$  in a  $1 \times 10^{-3}$  M  $Na_2S \cdot 9H_2O$  Solution

pH	$S^{--}$ , mg/l	$HS^-$ , mg/l	$H_2S$ , mg/l
6.8	$1.54 \times 10^{-7}$	12.7	20.9
7.5	$1.52 \times 10^{-6}$	25.8	8.24
8.3	$1.22 \times 10^{-5}$	31.42	1.62
9.0	$6.4 \times 10^{-5}$	33.0	$3.4 \times 10^{-1}$
10.0	$6.4 \times 10^{-4}$	33.0	$3.4 \times 10^{-2}$
10.9	$5.7 \times 10^{-3}$	33.0	$4.27 \times 10^{-3}$

It will be noted that the concentration of  $S^{--}$  increases with increasing pH and that the concentration of  $HS^-$  is effectively independent of pH. The concentration of  $H_2S$ , however, decreases rapidly with increasing pH with  $\log (H_2S)$  giving a linear relation to pH of a similar form to the observed adsorption (Fig. 7). This relationship would indicate that adsorption of  $H_2S$  is probably mainly responsible for the adsorption behaviour which was observed.

In the case of adsorption from phosphoric acid solutions, the pH adjustment was made using a dilute sodium hydroxide solution. Phosphoric acid, when being neutralized in this way, may be regarded as a mixture of three separate mono-basic acids of widely differing strengths, with three stages of neutralization occurring, corresponding to the strong acid  $H_3PO_4$ , the weak acid  $H_2PO_4^-$  and the very weak acid  $HPO_4^{--}$ . From a knowledge of the potentiometric titration curve of  $0.85 \times 10^{-3} M H_3PO_4$  against  $0.01 N NaOH$ , it is possible to calculate the amounts of the various phosphorus-containing species present at any given pH. This is shown in Fig. 8 for  $H_3PO_4$ ,  $H_2PO_4^-$ ,  $HPO_4^{--}$  and  $PO_4^{---}$ . The sum of the curves for the concentrations of  $H_2PO_4^-$  and  $HPO_4^{--}$  follows closely the observed results for the adsorption on the three sulphide minerals shown in Figs. 5 and 6. Thus, the adsorption curves would seem to arise in this case from the adsorption of  $H_2PO_4^-$  and  $HPO_4^{--}$  in their respective pH ranges and would indicate that the other phosphorus-containing species are not adsorbed.

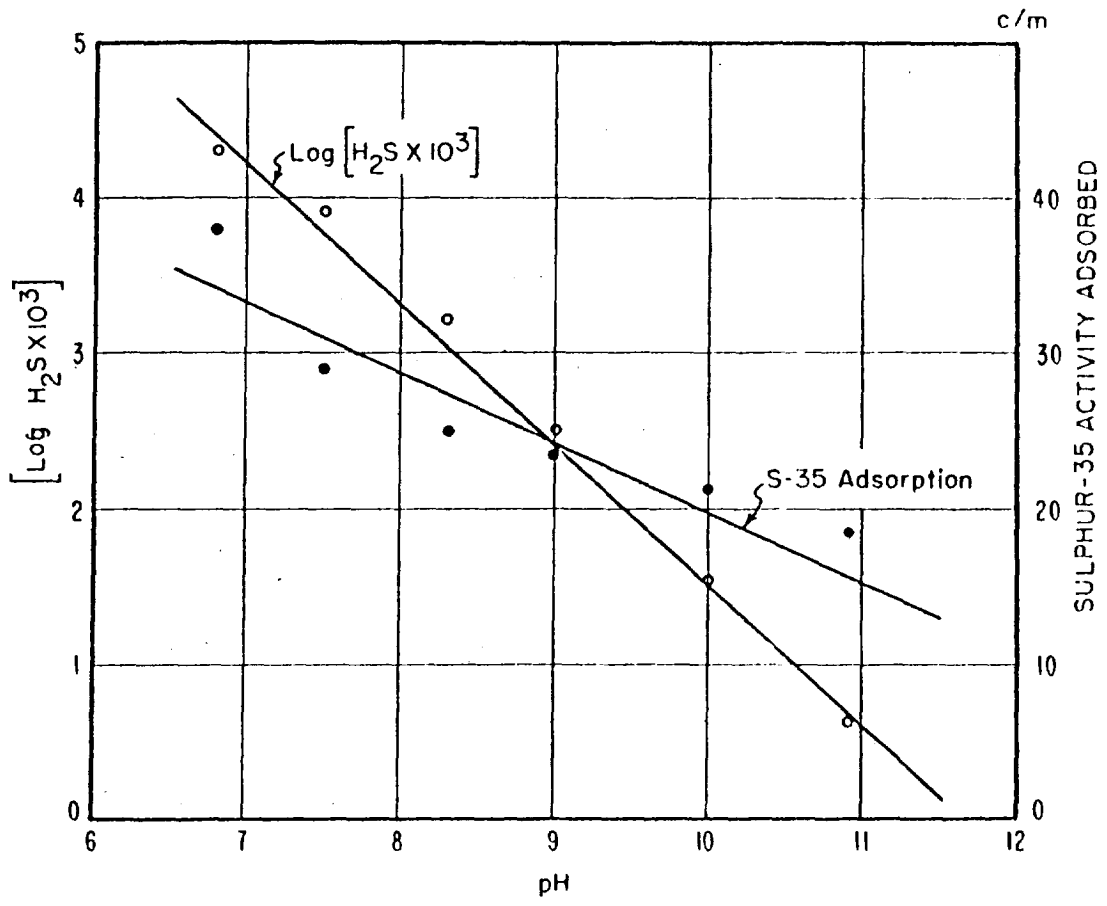


FIGURE 7- DEPENDENCE OF SULPHUR-35 ADSORPTION ON PYRITE, AND LOG  $[\text{H}_2\text{S}]$ , ON pH, IN A  $10^{-3}$  M  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  SOLUTION.

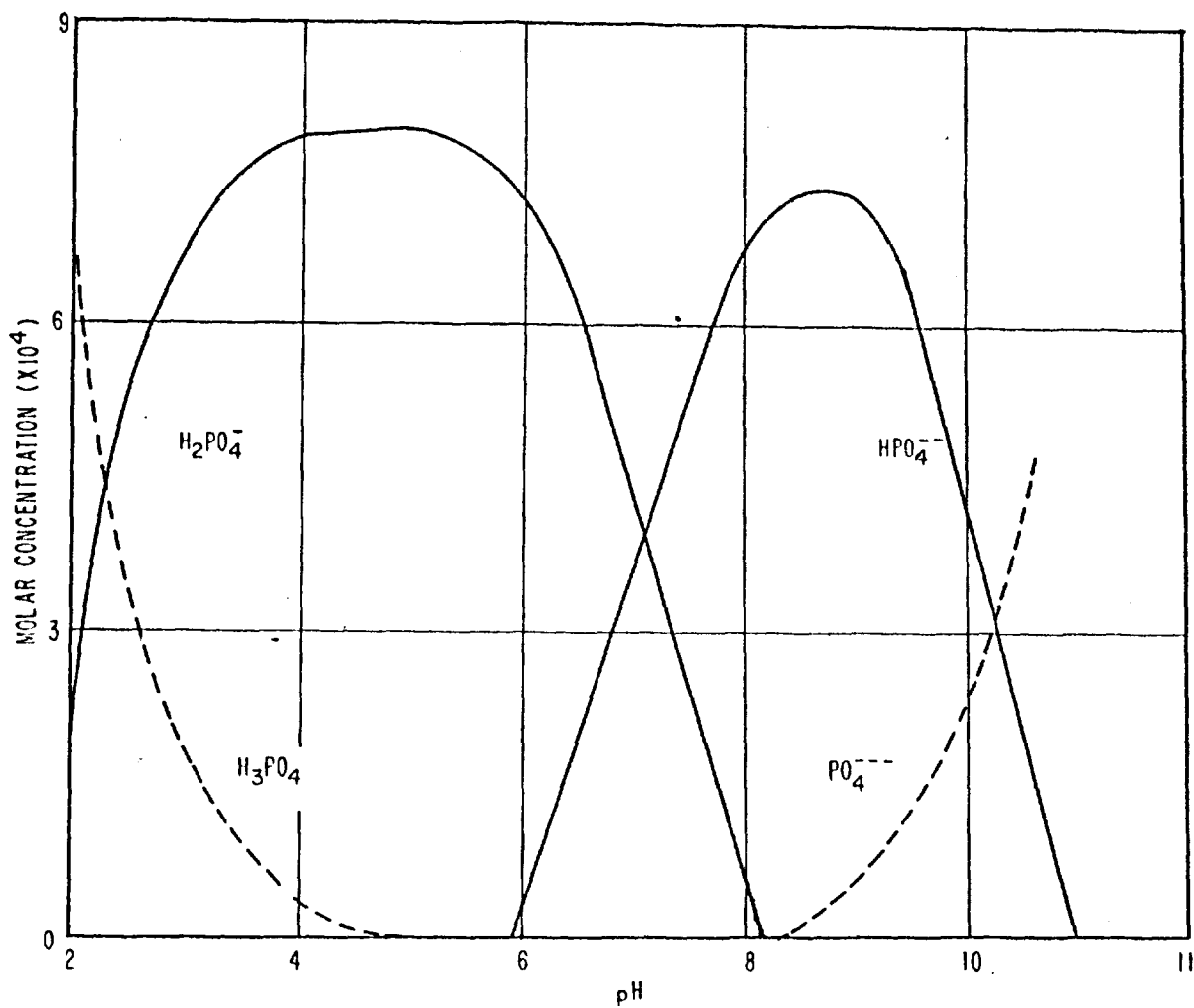


FIGURE 8 - CONCENTRATION OF  $H_3PO_4$ ,  $H_2PO_4^-$ ,  $HPO_4^{2-}$  AND  $PO_4^{3-}$  IN  $0.85 \times 10^{-3} M H_3PO_4$  AS A FUNCTION OF pH.

### ACKNOWLEDGMENTS

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### REFERENCES

- (1) Gaudin, A.M., Flotation, 2nd ed., McGraw-Hill Book Company, New York, (1957).
- (2) Eichholz, G.G. and Roberts, W.N., Proceedings, Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 19, 240 (1958).
- (3) Eichholz, G.G., Muir, W.B., Bennett, M.J.S., Wild, J.D., Lawton, C. and Mostowy, S., Trans. Can. Inst. Mining Met., 60, 63 (1957).
- (4) Bethge, P.O., Analytica Chim. Acta, 10, 310 (1954).
- (5) Jellinek, K. and Cyerwinski, J., Z. Physik. Chem., 102, 438 (1922).

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